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## Abstract

## Full Text

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# PROTOLYSIS OF DIBENZYLMERCURY BY THE $S_E1$ MECHANISM

Recently, in our laboratory, using as an example the isotopic exchange of organomercury compounds (ethyl ester of $\alpha$-bromomercuriphenylacetic acid and $p$-nitrobenzylmercury bromide) with bromine mercury labeled with $Hg^{203}$ in dimethyl sulfoxide (DMSO), the first cases were found of an electrophilic substitution reaction at a saturated carbon atom proceeding by a unimolecular $S_E1$ mechanism ([1,2]). However, in all other solvents investigated, the reaction takes place by a bimolecular $S_E2$ mechanism.

In the present work, continuing the study of the mechanism of protolysis of organomercury compounds ([3]), we investigated the acid cleavage of dibenzylmercury (DBM) under the action of HCl under conditions in which only one radical is replaced

$$(C_6H_5CH_2)_2Hg + HCl \rightarrow C_6H_5CH_3 + C_6H_5CH_2HgCl.$$

In view of the high lability of the bond

$$-C-Hg-$$

in DBM, we hoped to obtain the first example of an $S_E1$-type reaction at a saturated carbon atom in the protolysis of organometallic compounds. Indeed, it turned out that in DMSO the reaction proceeds according to first kinetic order, and, upon replacing HCl by DCl, no kinetic isotope effect was observed. This indicates that, with an overall first order, the reaction is first order in DBM and zero order in acid. The kinetics of the reaction was also investigated in a number of other solvents: dimethylformamide (DMF), aqueous (5%) acetonitrile, tetrahydrofuran, and butanol.

The kinetic study of the reaction was carried out titrimetrically by following the decrease in the concentration of chloride ions. To a thermostated solution of DBM, with stirring, there was added a solution of hydrogen chloride of equal concentration, preheated to the same temperature. The temperature of the experiment was maintained with an accuracy of $\pm 0.1^\circ$. The moment of addition of the second reagent was taken as the start of the reaction. At definite time

intervals, a certain volume of the reaction mixture (0.1–1.0 ml) was withdrawn, poured into 10 ml of methanol, and the amount of chloride ions was determined mercurimetrically: by titration with an acidified solution of mercuric nitrate (0.0008–0.01 mol/l) in aqueous methanol (95% methanol by volume) ([4]) until the appearance of the coloration characteristic of the complex of divalent mercury with diphenylcarbazone.

The reaction studied proved to be unimolecular not only in DMSO, but also in all the other solvents used by us: in all cases the first-order rate constant of the reaction was well maintained.

This result is not in agreement with the data of the work of Nerdel and Makower ([5]) on the protolysis of DBM in dioxane, who obtained a second kinetic order.

The rate constant was calculated from the half-life, determined graphically from anamorphoses of the kinetic curves. For some solvents (DMSO, DMF, $CH_3CN$) the study was carried out at several temperatures. Examples of logarithmic anamorphoses are giv–

data for the protolysis reaction of DBM in DMF (Fig. 1). The data obtained are given in Table 1.

From the temperature dependence of the reaction rate constant (Fig. 2), the energies and entropies of activation for the protolysis of DBM by hydrogen chloride were determined (Table 1).

Thus, we have the first example of a compound whose cleavage in different solvents, differing strongly in their polarity, proceeds exclusively as an $S_E1$-type reaction. We assume that this is a consequence of the exceptional lability of the bond

$$-\mathrm{C}-\mathrm{Hg}-$$

in dibenzylmercury. The reaction mechanism may be represented as follows: in the first (slow) stage of this reaction, ionization of the organomercury compound occurs with formation of an ion pair, which then in the fast stage interacts with hydrogen chloride

**Fig. 1.** Plots of the dependence $\lg C_0/C = f(r)$ for the protolysis of $(C_6H_5CH_2)_2Hg$ in $HCON(CH_3)_2$

$$\text{a)}\quad (C_6H_5CH_2)_2Hg \overset{\text{slow}}{\rightleftharpoons} C_6H_5\overset{\ominus}{C}H_2 : \overset{\oplus}{H}gCH_2C_6H_5,$$

$$\text{b)}\quad C_6H_5\overset{\ominus}{C}H_2 : \overset{\oplus}{H}gCH_2C_6H_5 + HCl \xrightarrow{\text{fast}} C_6H_5CH_3 + C_6H_5CH_2HgCl.$$

We studied the effect of water additions on the rate of protolysis of DBM in acetonitrile at 50°. As in other protolysis reactions of organomercury compounds,

an increase in the water content in the solvent led to a decrease in the reaction rate, although the first-order rate constant continued to be well maintained.

Table 2 gives the half-lives ($\tau_{1/2}$) and the rate constants for the protolysis of DBM at 50° in acetonitrile with different water contents and in absolute acetonitrile (obtained by extrapolation to $[H_2O] = 0$).

**Fig. 2.** Plots of the dependence $\lg K_1 = f(1/T)$ for the protolysis of $(C_6H_5CH_2)_2Hg$

The inhibiting action of water can be explained only by its action on the HCl molecule, since, taking into account the monomolecular character of the reaction, it may be asserted that increasing the polarity of the medium should facilitate ionization of DBM. It is known that in bimolecular protolysis the reaction rate also decreases with increasing water content [3]. This is connected with the fact that the attacking agent in the reaction is molecular HCl. In this case, at small additions of water the reaction rate decreases because hydrate shells are formed around HCl molecules, and at higher water content—because of increased dissociation of HCl.

In our case of a monomolecular reaction, inhibition by additions of water forces one to assume the presence of catalysis of the reaction by hydrogen chloride in molecular form, i.e., the formation, in the transition state, of a definite coordination between DBM and HCl molecules. Such coordi-

tion (not detected in kinetic measurements) promotes ionization of the C—Hg bond in DBR and the formation of a larger number of ion pairs. Additions of water, however, decrease the "effectiveness" of HCl in the above-mentioned sense and lower the concentration of ion pairs.

**Table 1**

| Solvent | Electrophilic agent | $t$, °C | $[DBR] = [HCl] \cdot 10^2$, mol/l | $\tau_{1/2}$, min | $K_1 \cdot 10^4$, $sec^{-1}$ | $E^{\neq}$, kcal/mol | $\lg A$ | $\Delta S^{\neq}$, e.u. |
|---|---|---|---|---|---|---|---|---|
| DMF | HCl | 40 | 1.75 | 196 | 0.589 | 14.5 | 5.95 | −33.3 |
| DMF | HCl | 40 | 3.0 | 196 | 0.589 | 14.5 | 5.95 | −33.3 |
| DMF | HCl | 40 | 3.5 | 196 | 0.589 | 14.5 | 5.95 | −33.3 |
| DMF | HCl | 45 | 2.9 | 135 | 0.856 | 14.5 | 5.95 | −33.3 |
| DMF | HCl | 50 | 3.6 | 95 | 1.21 | 14.5 | 5.95 | −33.3 |
| DMF | HCl | 50 | 1.8 | 95 | 1.21 | 14.5 | 5.95 | −33.3 |
| DMF | HCl | 55 | 2.9 | 67 | 1.71 | 14.5 | 5.95 | −33.3 |
| DMF | HCl | 60 | 3.8 | 48 | 2.4 | 14.5 | 5.95 | −33.3 |
| DMSO | DCl | 60 | 2.76 | 220 | 0.519 | 16.7 | 6.7 | −29.9 |
| DMSO | HCl | 65 | 2.2 | 158 | 0.73 | 16.7 | 6.7 | −29.9 |
| DMSO | DCl | 70 | 2.76 | 112 | 1.03 | 16.7 | 6.7 | −29.9 |
| DMSO | HCl | 70 | 2.2 | 112 | 1.03 | 16.7 | 6.7 | −29.9 |

| Solvent | Electrophilic agent | $t$, °C | $[DBR] = [HCl] \cdot 10^2$, mol/l | $\tau_{1/2}$, min | $K_1 \cdot 10^4$, $sec^{-1}$ | $E^{\neq}$, kcal/mol | lg $A$ | $\Delta S^{\neq}$, e.u. |
|---|---|---|---|---|---|---|---|---|
| DMSO | HCl | 75 | 2.2 | 79 | 1.46 | 16.7 | 6.7 | −29.9 |
| DMSO | HCl | 80 | 2.2 | 55 | 2.08 | 16.7 | 6.7 | −29.9 |
| DMSO | HCl | 80 | 2.2 | 55 | 2.08 | 16.7 | 6.7 | −29.9 |
| $CH_3CNHCl$ (5 mol. % $H_2O$) | | 40 | 2.13 | 41.7 | 2.78 | 12.7 | 5.3 | −36.3 |
| $CH_3CNHCl$ (5 mol. % $H_2O$) | | 43 | 2.13 | 34 | 3.4 | 12.7 | 5.3 | −36.3 |
| $CH_3CNHCl$ (5 mol. % $H_2O$) | | 45 | 2.13 | 30 | 3.8 | 12.7 | 5.3 | −36.3 |
| $CH_3CNHCl$ (5 mol. % $H_2O$) | | 47 | 2.13 | 27 | 4.27 | 12.7 | 5.3 | −36.3 |
| $CH_3CNHCl$ (5 mol. % $H_2O$) | | 50 | 2.13 | 22 | 5.24 | 12.7 | 5.3 | −36.3 |
| THF | HCl | 45 | 5.9 | 75 | 1.54 | | | |
| *n*-$C_4H_9OH$ | HCl | 40 | 0.56 | 80 | 1.44 | | | |

The phenomenon of catalysis once again emphasizes the conditional nature of the division of electrophilic substitution reactions into $S_E1$ and $S_E2$ on the basis of kinetic measurements.

It is natural to expect that the influence of water on the catalytic ability of HCl in the case of a monomolecular reaction will be considerably weaker than in cases where HCl is the reagent. Indeed, comparison of the data on the influence of water on the rate of reactions of the $S_E2$ and $S_E1$ types confirms this consideration: whereas in the bimolecular protolysis of benzylmercuric chloride in

dioxane (3) a twentyfold excess of water causes the reaction rate constant to fall by half, and a fiftyfold excess stops it altogether, in our case of monomolecular protolysis of DBR in $CH_3CN$ the reaction rate constant falls by a factor of only two with a fiftyfold excess of water, and at the ratio $[H_2O]/[HCl] = 306$ it falls by a factor of 6–7.

**Table 2**

| $[DBR] = [HCl] \cdot 10^2$, mol/l | $H_2O$ content (in mole percent) | $[H_2O]/[HCl]$ | $\tau_{1/2}$, min | $K_1 \cdot 10^4$, $sec^{-1}$ |
|---|---|---|---|---|
| – | 0 | 0 | 12 | 9.6 |
| 2.13 | 5 | 46.2 | 22 | 5.24 |
| 2.15 | 15 | 146.6 | 55 | 2.096 |
| 1.86 | 25 | 306 | 77 | 1.5 |

The hypothesis of the presence of catalysis in the case of DBR protolysis makes it possible to explain the series of solvent effects on the reaction rate that we obtained, which does not correspond to their ionizing ability. Indeed, the reaction proceeds faster in acetonitrile and DMF than in DMSO, in which ionization of the organomercury compound undoubtedly occurs more strongly. The overall series of solvent effects appears as follows:

$$CH_3CN > n\text{-}C_4H_9OH > THF > DMF > DMSO$$

| $K_1 \cdot 10^4$ at 40° | 2.78 (5% $H_2O$) | 1.44 | 1.54 (45°) | 0.589 | 0.111 |
|---|---|---|---|---|---|

If, however, one takes into account that the strength of solvent complexes with hydrogen chloride apparently changes in the same order, then the following conclusion suggests itself: the weaker the solvent · HCl complex, the stronger the catalytic action of HCl in the sense of ionization of the

C—Hg

bond, and the more rapidly the protolysis of DBM proceeds in this solvent.

In this case it is easy to explain the observed increase in the activation energy on going from $CH_3CN$ to DMSO, which is associated with the necessity of an additional expenditure of energy to break the HCl·solvent bond.

Proceeding from the hypothesis of coordination of hydrogen chloride with DBM, it is logical to suppose that an excess of HCl relative to DBM should cause an

increase in the reaction rate (catalysis), although this contradicts the classical scheme of monomolecular substitution. Indeed, we found that the rate constant for the protolysis of DBM in $CH_3CN$ (5% $H_2O$) at 45° is directly proportional to the ratio [HCl]/[DBM]. An analogous phenomenon had already been found ([6]) in the monomolecular protolysis of phenylmercury bromide in 70% aqueous dioxane. Its cause is unknown to us and is currently being studied.

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*Note: Figure translations are in progress. See original paper for figures.*